CONCENTRATION AND TIME DEPENDENCE OF MIGRATION OF PCDD/PCDF FROM PAPER-BOARD CARTONS INTO MILK

O. Päpke, M. Ball, A.Z. Lis

ERGO Forschungsgesellschaft mbH
Albert-Einstein-Ring 7
2000 Hamburg 50
Federal Republic of Germany

ABSTRACT

In a series of investigation, we have studied the process of migration of PCDD/PCDF from paper-board cartons into milk.
We report on the influence of:

- storage times
- PCDD/PCDF levels in paper-boards
- fat contents of milk

on the PCDD/PCDF concentrations in the stored milk. Additionally, the PCDD/PCDF levels in 14 unstored milk samples from different regions of Germany are presented.

KEY WORDS

Polychlorinated dibenzodioxins (PCDD), polychlorinated dibenzofurans (PCDF), migration, paper-board cartons, cow milk.

INTRODUCTION

The migration of PCDD/PCDF from paper-board material, made of bleached pulp, into the milk stored was reported for the first time by Ryan et al. (1) at the Dioxin Conference 1988 in Umea. This peculiar phenomenon of PCDD/PCDF transport through the polyethylene layers of the cartons into milk has been confirmed in a series of experiments (2) to (7).
The results presented in this paper originate from a number of investigations carried out at various dairies in Germany.

STUDY DESIGN

The experiments took place at dairies located in Hamburg, Köln, Flensburg, Kiel and Schrozberg. In each of the dairies the sampling involved filling milk into bottles as well as into paper-board cartons of interest. Empty cartons, bottled milk and carton-packed milk were immediately sent to the lab in Hamburg and subsequently stored. The following storage parameters were provided:

	Temperature	Storage Time
Milk, 1.5 % and 3.5 % fat content	8 °C	6 days
Cream, 30 % fat content	20 °C	21 days

After appropriate storage-time, the contents of 5 individual cartons were mixed together, in order to obtain an average sample.

These samples were poured into glass bottles which were closed immediately thereafter with teflon-lined caps and stored prior to analysis at - 35 °C. In order to make the PCDD/PCDF migration more distinct, the investigations involved cartons produced in 1988, which would no longer be in current use. According to the carton producers, since May 1989 the PCDD/PCDF levels in milk containers do not exceed 1 ppt TEQ.

EXPERIMENTAL

For extraction, 20 g shredded paper-board cartons, 100 g milk or 10 g cream were used. Prior to the extraction, the samples were spiked with 13-C-UL internal standards. For each of the congener groups, at least one internal standard was introduced with exception of OCDF.
The carton samples were extracted with a Soxhlet for 20 hours with 95 % ethanol. The milk and cream extractions were carried out according to the method of Fürst et al. (8) (9) involving ethanol, diethylether and pentane with the presence of potassium oxalate. This procedure was followed by two consecutive pentane extractions. After shaking the extract with water, drying the organic phase with sodium sulphate and evaporating the extract in a rotary evaporator, the fat content of the milk was determined gravimetrically.

The clean up of the carton and milk extracts was performed by using a multicolumn system applying:

- silica gel / potassium silicate / H_2SO_4 - silica gel
- carbon on glass fibre (10)
- cesium silicate / H_2SO_4 - silica gel
- alumina

The subsequent measurements were carried out by means of HRGC/MS involving a 60 m SE-54 glass or DB-5 fused-silica capillary column, coupled with a VG 7035 mass spectrometer. For each compound, at least two isotope masses were measured. The quantification was carried out by comparison to an external standard mixture taking into account the recoveries of the internal standards.
The detection limit of 2.3.7.8-TCDF in milk fat and in paper-board samples is usually between 0.1 and 0.2 ppt.

RESULTS AND DISCUSSION

The results of the PCDD/PCDF determinations in cartons, unstored milk/cream and stored milk/cream are presented in Table 1.
In the experiments with carton stored milk, migration of the paper-board-bound PCDD/PCDF is obvious. The levels measured in some of the cartons were very low resulting in milk concentrations approaching the detection limits.
The migration rates are most distinct in the case of the paper-board cartons made of pulp and produced in 1988, which would not be presently used. They show concentrations of more than 8 ppt TEQ. On contrary to this in the experiments with cream stored in relatively high-level carton (13.9 ppt TEQ) only a small migration was noticed even after 21 days storage time. This observation corresponds well to the results of Oehme et al. with cream (5).

The migration rates of PCDD/PCDF from cartons into milk can be calculated for each of the experiments from the following quantities:

- PCDD/PCDF levels in the cartons
- the carton weight (about 27 g each)
- the milk weight (1000 g)
- the differences of PCDD/PCDF concentrations in milk at the beginning and at the end of storage

Depending on absolute concentration values, the particular migration rates show marked fluctuations - mostly in the case of low-level cartons and nearing detection limits. For this reason, a regression calculus involving the absolute PCDD/PCDF levels (x) and concentration differences in milk (y) was carried out.
For 2.3.7.8-TCDF the migration rate of 10.3 % and for all the PCDD/PCDF determined 7.6 % (in terms of TEQ) were found.
The functional relations are presented in Fig. 1 and Fig. 2 .

The time dependance of the migration processes can be interpreted through the data in Table 2. A distinct increase of 1.2.7.8-TCDF and 2.3.7.8-TCDF levels in stored milk is visible first after 6 days of storage.

PCDD and PCDF in paperboard containers (CARTON), unstored and stored milk/cream
Levels in ng/kg (ppt), for milk/cream: fat weight basis

	CARTON, > 10 ppt TEQ *						CARTON, < 5 ppt TEQ								CARTON < 1 ppt TEQ							CARTON	
	A	B	C	D	Mean	Range	E	F	G	H	I	J	Mean	Range	K	L	M	N	O	Mean	Range	P	Q *
2.3.7.8-TCDD	1.4	16	13	12	10.6	1.4 - 16	1.3	0.4	1.1	1.7	1.1	1.4	1.2	0.4 - 1.7	n.d.	0.5	0.3	0.3	0.3	0.3	n.d. - 0.5	0.3	6.3
2.3.7.8-TCDF	101	161	137	160	140	101 - 161	16	15	14	25	5.2	5.6	13.5	5.2 - 25	< 0.1	2.6	3.2	3.2	1.1	1.8	<0.1 - 3.2	1.5	71
1.2.7.8-TCDF	30	73	63	81	62	30 - 81	3.3	5.0	7.1	17	1.7	2.0	6.0	1.7 - 17	< 0.1	0.8	1.4	1.4	0.5	0.7	<0.1 - 1.4	0.4	24
TEQ (FHO)	12.2	33.5	28.5	30.2	26.1	12.2 - 33.5	3.0	2.8	3.9	4.5	1.9	2.2	3.1	1.9 - 4.5	0.23	0.94	0.80	0.80	0.66	0.66	0.23 - 0.94	0.54	13.9
	MILK, 0-days						MILK, 0-days								MILK, 0-days							CREAM, 0-days	
2.3.7.8-TCDD	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<0.1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d. - <0.1	n.d.	n.d.	n.d.	n.d.	0.4	n.d.	n.d. - 0.4	n.d.	n.d.
2.3.7.8-TCDF	< 0.1	0.2	n.d.	0.2	0.1	n.d. - 0.2	0.5	0.1	0.2	0.2	n.d.	0.2	0.2	n.d. - 0.5	< 0.1	0.2	<0.1	0.5	0.2	0.2	<0.1 - 0.5	<0.2	<0.2
1.2.7.8-TCDF	< 0.1	<0.1	n.d.	n.d.	<0.1	n.d. - < 0.1	n.d.	n.d.	n.d.	<0.1	n.d.	n.d.	n.d.	n.d. - <0.1	< 0.1	n.d.	<0.1	n.d.	<0.1	<0.1	n.d. - 0.1	n.d.	n.d.
TEQ (FHO)	0.70	0.21	0.15	0.29	0.34	0.15 - 0.70	0.65	0.80	0.64	0.21	0.15	0.29	0.46	0.15 - 0.80	0.49	0.48	0.49	0.56	0.95	0.59	0.48 - 0.95	0.25	0.25
	MILK, 6-days						MILK, 6-days								MILK, 6-days							CREAM, 21-days	
2.3.7.8-TCDD	< 0.2	<0.3	0.4	0.7	0.4	<0.2 - 0.7	n.d.	<0.1	n.d.	<0.1	<0.1	<0.1	<0.1	n.d. - <0.1	n.d.	0.1	n.d.	n.d.	0.4	0.1	n.d. - 0.4	n.d.	n.d.
2.3.7.8-TCDF	6.9	11	16	15	12.2	6.9 - 16	1.7	0.7	1.8	1.4	0.4	0.3	1.1	0.3 - 1.8	<0.2	0.4	0.4	0.8	0.5	0.5	<0.2 - 0.8	0.1	0.6
1.2.7.8-TCDF	3.0	6.6	10	11	7.7	3.0 - 11	0.8	0.4	1.1	1.0	0.2	0.1	0.6	0.1 - 1.1	n.d.	0.1	0.3	<0.3	<0.1	0.2	n.d. - 0.3	<0.1	0.2
TEQ (FHO)	1.7	1.8	2.4	2.7	2.2	1.7 - 2.7	0.65	0.74	1.1	0.45	0.36	0.38	0.61	0.36 - 1.1	0.61	0.73	0.64	0.54	1.1	0.72	0.54 - 1.1	0.28	0.39
fat content % milk/cream	3,5	3,5	3,5	3,5			1,5	3,5	1,5	3,5	3,5	3,5			3,5	3,5	3,5	1,5	3,5			30	30

* = From Production 1988, no more in use; n.d. = not detected

Table 1

PCDD/PCDF in Cow Milk

Levels in ng/kg (ppt), fat weight basis

	HH-1	HH-2	HH-3	HH-4	HH-5	KÄ-1	KÄ-2	KÄ-3	KÄ-4	Fl-1	FL-2	FL-3	KI	Schr	Mean	Range
2.3.7.8-Tetra-CDD	n.d. (0,1)	n.d. (0,1)	< 0,2	n.d. (0,2)	0,4	< 0,1	n.d. (0,3)	n.d. (0,2)	0,2	n.d. (0,1)	n.d. (0,1)	n.d. (0,1)	n.d. (0,3)	n.d. (0,2)	0,1	n.d. (0,1) - 0,4
1.2.3.7.8-Penta-CDD	< 0,3 (0,3)	< 0,4	1,0	< 0,3	0,5	0,2	0,8	0,2	0,5	n.d. (0,2)	n.d. (0,1)	n.d. (0,2)	n.d. (0,4)	n.d. (0,4)	0,3	n.d. (0,1) - 1,0
1.2.3.4.7.8-Hexa-CDD	n.d. (0,3)	n.d. (0,8)	< 0,4	n.d. (0,4)	n.d. (0,5)	< 0,4	n.d. (0,4)	n.d. (0,3)	n.d. (0,3)	n.d. (0,3)	n.d. (0,2)	0,2	n.d. (0,4)	n.d. (0,3)	n.d.	n.d. (0,2) - < 0,4
1.2.3.6.7.8-Hexa-CDD	1,2	n.d. (0,8)	1,1	0,7	0,6	0,6	< 0,4	n.d. (0,3)	0,8	< 0,3	0,3	0,2	n.d. (0,4)	0,4	0,4	n.d. (0,3) - 1,2
1.2.3.7.8.9-Hexa-CDD	< 0,3 (0,3)	n.d. (0,8)	0,7	n.d. (0,4)	n.d. (0,6)	< 0,4	n.d. (0,6)	< 0,3	n.d. (0,3)	n.d. (0,3)	< 0,2	n.d. (0,1)	n.d. (0,4)	n.d. (0,3)	0,1	n.d. (0,3) - 0,7
TOTAL Hexa-CDD	1,6	n.d. (0,8)	2,0	0,7	< 0,6	1,0	< 0,4	< 0,3	0,8	< 0,3	0,4	0,4	n.d. (0,4)	0,4	0,5	n.d. (0,4) - 2,0
1.2.3.4.6.7.8-Hepta-CDD	1,8	2,7	3,2	1,5	3,1	1,4	3,9	0,8	0,8	0,8	0,7	0,7	2,5	1,3	1,6	0,7 - 3,2
Octa-CDD	4,4	10	3,6	6,5	2,3	3,8	2,7	< 4	0,9	4,2	2,9	2,2	11	3,8	4,3	0,9 - 11
2.3.7.8-Tetra-CDF	< 0,3	0,5	0,7	0,2	0,2	0,1	0,2	0,2	0,1	0,2	n.d. (0,1)	< 0,1	< 0,2	0,2	0,2	n.d. (0,1) - 0,7
1.2.3.7.8-Penta-CDF	n.d. (0,1)	< 0,4	< 0,3	n.d. (0,2)	0,7	< 0,2	< 0,2	< 0,2	n.d. (0,1)	< 0,2	n.d. (0,1)	< 0,1	n.d. (0,4)	n.d. (0,2)	0,1	n.d. (0,1) - 0,7
2.3.4.7.8-Penta-CDF	0,9	1,6	4,1	1,1	1,3	2,0	1,7	0,4	1,7	0,5	0,4	0,5	0,7	1,1	1,3	0,4 - 4,1
TOTAL Penta-CDF	0,9	1,8	4,3	1,1	2,0	2,1	1,8	0,5	1,7	0,6	0,4	0,6	0,7	1,1	1,4	0,4 - 4,3
1.2.3.4.7.8-Hexa-CDF	0,4	1,4	2,2	0,8	0,8	1,1	1,0	0,5	0,8	0,3	0,2	0,2	< 0,4	0,3	0,8	0,2 - 2,2
1.2.3.6.7.8-Hexa-CDF	0,1	1,1	1,6	0,8	0,7	0,9	0,6	0,3	0,7	0,2	0,2	0,2	< 0,4	0,3	0,6	0,2 - 1,6
1.2.3.7.8.9-Hexa-CDF	n.d. (0,3)	n.d. (0,4)	n.d. (0,2)	n.d. (0,3)	n.d. (0,2)	n.d. (0,2)	n.d. (0,3)	n.d. (0,2)	n.d. (0,1)	n.d. (0,2)	n.d. (0,1)	n.d. (0,1)	n.d. (0,4)	< 0,2	n.d.	n.d. (0,1) - < 0,2
2.3.4.6.7.8-Hexa-CDF	0,3	0,8	0,5	0,5	0,8	0,5	0,7	< 0,2	0,5	0,2	0,1	0,1	< 0,4	0,2	0,4	< 0,2 - 0,8
TOTAL Hexa-CDF	1,7	3,3	4,3	2,1	2,8	2,5	2,5	0,9	2,0	0,7	0,5	0,5	0,6	0,9	1,8	0,5 - 4,3
1.2.3.4.6.7.8-Hepta-CDF	0,9	2,5	1,6	0,6	1,8	0,7	1,0	< 0,3	0,4	0,3	< 0,2	0,2	< 0,5	< 0,2	0,7	< 0,2 - 2,5
1.2.3.4.7.8.9-Hepta-CDF	n.d. (0,4)	n.d. (1,0)	0,2	n.d. (0,3)	n.d. (0,6)	n.d. (0,3)	n.d. (0,4)	n.d. (0,3)	n.d. (0,2)	n.d. (0,2)	n.d. (0,2)	n.d. (0,2)	n.d. (0,5)	n.d. (0,2)	n.d.	n.d. (0,2) - 0,2
TOTAL Hepta-CDF	0,9	2,5	1,8	0,6	1,8	0,7	1,0	< 0,3	0,4	0,3	< 0,2	0,2	< 0,5	< 0,2	0,7	< 0,2 - 2,5
Octa-CDF	< 1,0	< 2,0	< 0,3	< 0,4	n.d. (1,0)	< 0,5	< 1,0	n.d. (4,0)	n.d. (0,2)	< 0,5	0,4	n.d. (0,3)	< 0,6	n.d. (0,4)	0,3	n.d. (0,2) - < 2,0
TOTAL PCDD (Cl > 4)	7,8	12,8	9,9	8,9	4,6	6,5	7,8	3,2	3,2	5,2	4,0	3,3	13,5	5,2	6,6	3,2 - 13,5
TOTAL PCDF (Cl > 4)	4,1	9,1	11,3	4,2	5,0	6,0	6,0	1,8	4,2	2,1	1,4	1,4	2,0	2,3	4,4	1,4 - 11,3
TOTAL PCDD/PCDF (Cl > 4)	11,9	21,8	21,2	13,1	9,6	12,5	13,8	5,0	7,4	7,3	5,4	4,7	15,5	7,5	11,0	4,7 - 24,8
TEQ (FMD)	0,49	0,84	1,60	0,48	0,95	0,80	0,64	0,25	0,73	0,21	0,15	0,17	0,25	0,29	0,55	0,15 - 1,6

Dairies locations: HH = Hamburg
Kö = Köln (Cologne)
Fl = Flensburg
Ki = Kiel
Schr = Schrozberg

n.d. = not detected, detection limit in ( )

Table 3

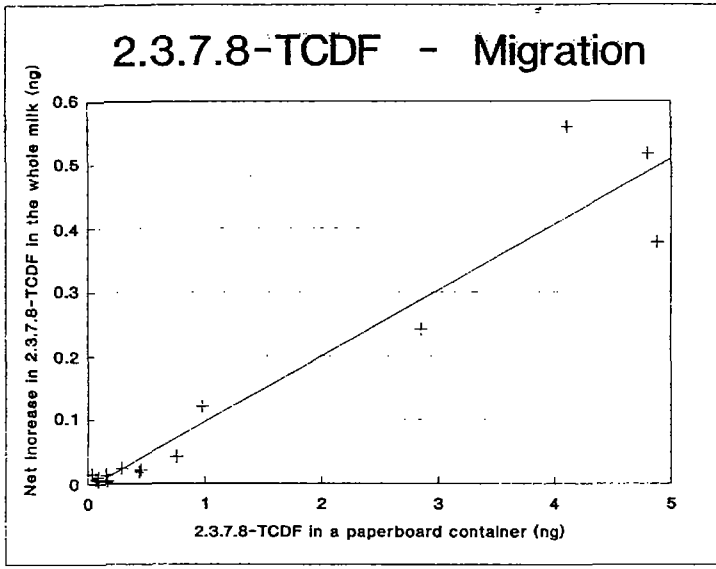

Figure 1

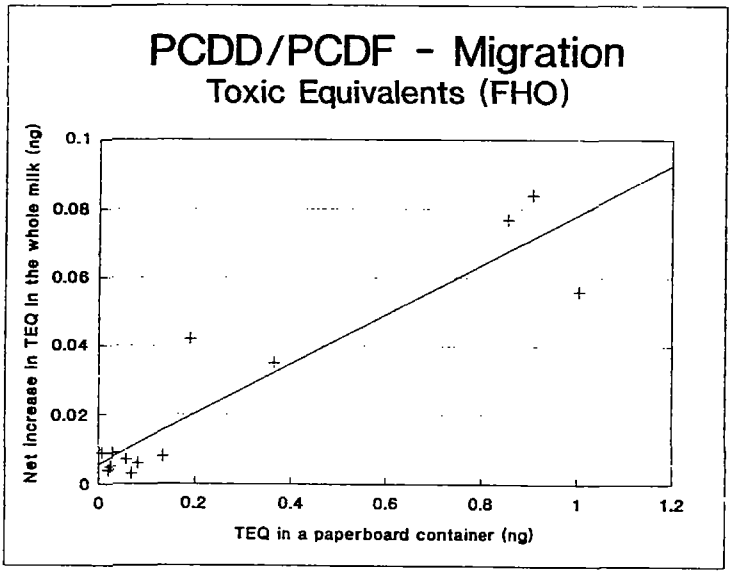

Figure 2

Table 2: Milk storage in paper-board containers (cartons)
Levels in ng/kg (ppt) in milk (fat weight based)

	Carton	Milk				
		Original	Storage time (days)			
			0	2	4	6
2.3.7.8-TCDD	0.3	n.d.(0.1)	n.d.(0.1)	< 0.1	n.d.(0.2)	n.d.(0.2)
2.3.7.8-TCDF	3.2	< 0.1	< 0.1	< 0.1	< 0.2	0.4
1.2.7.8-TCDF	1.4	< 0.1	< 0.1	< 0.1	< 0.3	0.3
TEQ	0.8	0.49	0.46	0.46	0.43	0.64

n.d. = not detected, detection limit in ( )

All the unstored milk samples investigated under this study (with sampling in glass bottles taking place at the filling tanks of the dairies mentioned) are compared in Table 3.
The mean PCDD/PCDF level of the 14 samples measured is 0.55 ppt TEQ, ranging from 0.15 ppt to 1.60 ppt TEQ. These values correspond well to those reported by Mathar et al. (2), with the mean concentration of 0.9 ppt TEQ and the level range of 0.6 - 1.6 ppt TEQ.

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